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A PRELIMINARY REPORT ON SOME MAGNETIC AND MÖSSBAUER SPECTROSCOPY INVESTIGATIONS OF WAITE AMULET TAILINGS

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Transport from Tailings

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A PRELIMINARY REPORT ON SOME MAGNETIC AND MOSSBAUER SPECTROSCOPY INVESTIGATIONS OF WAITE AMULET TAILINGS

by

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ABSTRACT

Studies of the magnetic behaviour of synthetic iron-oxide and -sulphide standards show that great care must be exercised when interpreting magnetic data from uranium tailings. A method proposed by Morris (1) using magnetic susceptibility data to monitor tailings appears to be based on an erroneous premise.

Mössbauer spectroscopy is able to provide direct identification and quantification of the iron-bearing species in tailings samples. Additional techniques such as laser Raman and infrared spectroscopy are required to provide complete characterization of the molecular species present.

The necessity of any monitoring technique to be not only accurately correlated with the physical and chemical changes in the tailings site, but also relevant to the study of the preceived environmental hazards is briefly discussed.

RAPPORT PRÉLIMINAIRE SUR QUELQUES ÉTUDES DE LA SENSIBILITÉ MAGNÉTIQUE ET LA SPECTROSCOPIE DE MÖSSBAUER EFFECTUÉES SUR LES RÉSIDUS DE WAITE AMULET

par

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RÉSUMÉ

Les études du comportement magnétique de l'oxyde et du sulfure de fer synthétique démontrent que c'est avec le plus grand soin qu'il faut interpréter les données sur la susceptibilité magnétique des résidus d'uranium. Il appert, en outre, que la méthode proposée par Morris (1), soit celle d'utiliser les données de la susceptibilité magnétique pour effectuer la surveillance des résidus, serait basée sur de fausses prémisses.

L'emploi de la spectroscopie de Mössbauer permet d'obtenir une identification directe ainsi que la quantification des espèces ferrifères trouvées dans les résidus. Des techniques additionnelles telles que la spectroscopie Raman au laser et la spectroscopie infrarouge sont nécessaires afin de d'obtenir la caractérisation complète des espèces moléculaires présentes.

Enfin, dans le présent rapport, on examine brièvement qu'il est non seulement nécessaire qu'une méthode de surveillance soit corrélée de façon précise avec les changements physiques et chimiques de l'emplacement des résidus, mais il faut aussi qu'elle soit appropriée à l'étude des dangers environnementaux prévus.

INTRODUCTION

Studies have been carried out within CANMET to elucidate the mechanism of evolution of uranium mine tailings. In order to minimize the environmental impact of tailings sites it is necessary to understand the physical and chemical changes which occur over extended time periods. One method which has been proposed as a useful tool to monitor *in situ* the variation in composition of these sites involves measuring the magnetic susceptibility of the tailings (1).

In this preliminary report we describe magnetization curves and Mössbauer spectroscopic measurements obtained from well characterized synthetic iron oxide and sulphide standards in addition to a specimen taken from a suite of samples from the Waite Amulet tailings site. Comparisons are made between this and other studies and the suitability of proposed monitoring techniques discussed. A full report on the series of Waite Amulet tailings WA20 - 1 to 20 is in preparation.

EXPERIMENTAL

Tailings samples were received as *ca.* 5 g quantities in glass specimen bottles. To ensure reproducibility of sampling the entire contents were emptied into an agate mortar and carefully ground. Smaller samples of the homogenized whole were taken for investigation. High purity synthetic magnetite, hematite, goethite and pyrrhotite were obtained from Alpha Products. Materials were checked by comparing their Mössbauer spectra with literature values.

MAGNETIC SUSCEPTIBILITY

Data were recorded using a vibrating sample magnetometer linked to an Apple IIe via an EG and G interface. Accurately weighed samples of *ca.* 150-200 mg were placed into a holder of known magnetic properties. The external magnetic field was varied continuously from 0 to 6000G, 6000G to -6000G and -6000G to 6000G to enable measurement of retentivity (remanence), coercivity and saturation moment in addition to magnetic susceptibility. Three separate experiments were performed with each tailings sample and an

accuracy of +/- ca. 2.5% achieved for values of susceptibility and saturated moment.

MÖSSBAUER SPECTROSCOPY

Measurements were made using an Austin Sciences instrument with a ca. 35 mCi γ-ray source of ^{57}Co in rhodium. Accurately weighed samples of ca. 400 mg were intimately mixed with vacuum grease and pressed to the appropriate absorber thickness. Spectra were velocity calibrated with a laser interferometer. Data were computer analyzed with a non-linear least squares program assuming pure Lorentzian line shapes and spectral parameters reported relative to α-Fe.

RESULTS

1. MAGNETIC SUSCEPTIBILITY

Table 1. Magnetic moments of standard iron compounds in different applied magnetic fields

	MAGNETITE	HEMATITE	PYRRHOTITE
Satd. moment/g^{-1}	84.0(7kG)	0.29(7kG)	14.0(6kG)
m(sat)-m(1.5kG)/g^{-1}	13.5	0.2	3.6
m(1.5kG↓)-m(1.5kG↑)/g^{-1}	0.65	0.2	0.94

The above table shows magnetic data recorded from our standard materials. (Note: hematite is antiferromagnetic with a ferrimagnetic contribution resulting from spin canting and therefore does not reach magnetic saturation in the fields used here.) It is evident that magnetite does not reach saturation in an external field of 1.5kG as reported by Morris (1). He uses 1.5kG as the threshold limit for "magnetite remanence" (induced magnetic moment) and the difference between remanence values at 1.5kG and 7.5kG as an indication of hematite remanence. Line two of the table shows that the contribution of magnetite (13.5 emu g^{-1}) to the increase in magnetisation is ca. 45 times greater than the contribution of hematite (0.2 emu g^{-1}) over the same field increment. Pyrrhotite may also contribute to the increase in magnetization, although the contribution per gram is only one quarter that of magnetite.

MÖSSBAUER SPECTROSCOPY

A typical spectrum is shown in Fig. 1. Mössbauer spectroscopy using a ^{57}Co source specifically detects iron and hence the spectrum represents only the iron-bearing species in the tailings. Five distinct iron compounds are readily identified and are shown coded in Fig. 1. While the present experiments alone cannot unambiguously identify doublets A and B, it is probable that doublet A arises from the presence of pyrite and doublet B from Fe(II) in a silicate species. Measurements at low temperature or in an external magnetic field would provide more unequivocal evidence, as would the use of infrared or Raman spectroscopy.

Computer fitting of recorded spectra allows compound identification and quantification from the areas under the curves which make up the complete spectrum. However, to enable rapid dissemination of this report heights of selected spectral peaks have been measured to give an indication of the concentration trends through the series of tailings. Plots of percentage spectral contribution of iron phases, along with data for the main iron-bearing species calculated from results of Petruk and Pinard (2) are given in Fig. 2-5.

Figures 2-5 suggest that our Mössbauer data do show some correlation with the mineralogical data (2), although in the absence of concentration standards and computer fitting of all the Mössbauer data only the trends are relevant. Nevertheless it should be emphasized that the Energy Dispersive Analysis of X-rays (EDX) used in the mineralogical study (2) yields only ratios of elements from which the molecular species are inferred. Indeed, oxygen is not detected by the CANMET apparatus. Mössbauer spectroscopy is able directly to provide phase analysis of the iron-bearing species and concentration profiles through the series of tailings. Complete analysis will appear in the later report.

DISCUSSION

Our magnetic data clearly show that magnetite does not reach saturation in an external field of only 1.5kG. Indeed, the magnetic moment is just 84% of the saturation moment. Thus, if hematite is present in tailings its contribution to the increase in magnetization between 1.5kG and 7.5kG is

negligable. Moreover, this is also the case for any material not exhibiting ferro- or strong ferrimagnetism. The only other material present to contribute to the change in magnetic moment is ferrimagnetic pyrrhotite. However, given the lower net moment per Fe atom this contribution is small compared to the increase in magnetic moment of magnetite as confirmed by our measurements. Therefore, it appears that the method proposed by Morris (1) to correlate magnetic measurements with magnetite/hematite ratios, and thereby the oxidation state of the tailings, is seriously flawed. It is important to note that while we have studied different tailings from those of Morris (1), our findings concerning his methodology are based on the magnetic behaviour of standard materials and hence have general validity. We do not comment on the composition of Morris' tailings.

If it is possible to develop a quick and easy technique for the assessment of tailings sites it is necessary to define precisely the physical and chemical chanages of interest and then correlate these accurately with the proposed method. This requires identification of the molecular species present in the tailings. We have demonstrated that Mössbauer spectroscopy is a powerful tool for direct analysis of iron-bearing phases. Other methods such as infrared and laser Raman spectroscopy are needed to provide a more complete description of the species present in the tailings.

Nevertheless, while it may be possible to characterize the tailings with respect to their molecular composition and to develop a technique for in situ monitoring, the relevance of the approach to the problem of tailings management needs to be determined. A more detailed discussed will be presented in a later report; however, a number of problems are evident.

1. To study changes in tailings sites a knowledge of the initial state of the tailings is desirable. It seems unlikely that dump sites would have started life as an homogeneous mixture. In the absence of records from the Waite Amulet tailings it is difficult to decide upon the likely composition of "unaltered" tailings. The possibility of using the deepest level of tailings as representing a least altered state appears to be negated by the considerable fluctuation known (3) to occur in the water table. In addition, the rate of transport of species from the upper levels through the body of the tailings is uncertain. Hence, some alteration of the composition of the base tailings may not be excluded.

2. What are the possible physical and chemical pathways for modification or transport of phases through the tailings? Magnetite is unlikely to undergo chemical modification in the tailings environment and is equally unlikely to have been formed from other species present. Thus it was probably present in the tailings originally and any change in the distribution is brought about by the material being washed down fissures. Goethite may dehydrate to hematite, but only at 200°C. Even then there is no change in oxidation state of Fe and little change in magnetic behaviour of the tailings. Pyrrhotite and pyrite may be oxidized to soluble iron sulphates which may then wash through the tailings, possibly with some reprecipitation. Certainly oxidation of pyrrhotite would result in a considerable change in the magnetic properties of this material, but this may be masked by the independent variation in magnetite concentration. Some locally reducing atmospheres caused by hydrogen sulphide generation from the classic reaction of acid on pyrite may add further complications. However, variation in the magnetization of the tailings probably results mainly from physical movement of magnetite and not from chemical modification of the tailings.

3. It is not clear how susceptibility measurements relate to the presence of uranium. There is some confusion in Morris' report (1) as to whether uranium is more or less likely to be found in the presence of magnetite. Careful consideration of the chemistry of uranium and the daughter nuclides and their relationship with the species measured by magnetic susceptibility seems advisable.

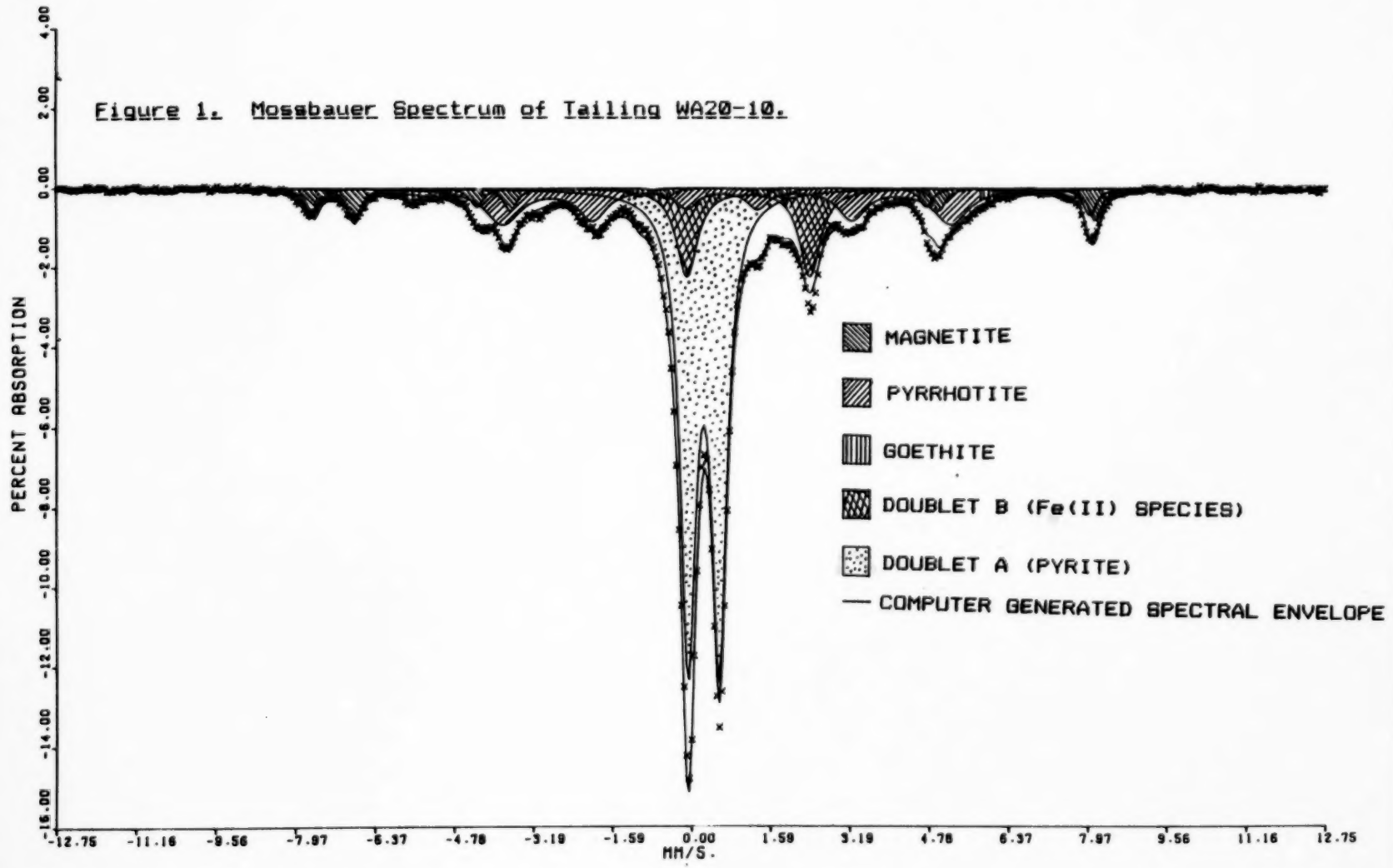
REFERENCES

1. Morris, W. "Measurement of magnetic susceptibility on tailings cores obtained from the Ontario Research Foundation Lysimeter Experiment"; DSS Contract No. OSQ84-00103.

2. Petruk, W. and Pinard, R.G. "Mineralogical and image analysis study of samples from core WA20 of the Waite Amulet tailings"; Division Report MSL 86-87 (IR); CANMET, Energy, Mines and Resources Canada; 1986.

3. Campbell, M. Private Communication.

Figure 1. Mossbauer Spectrum of Tailing WA20-10.



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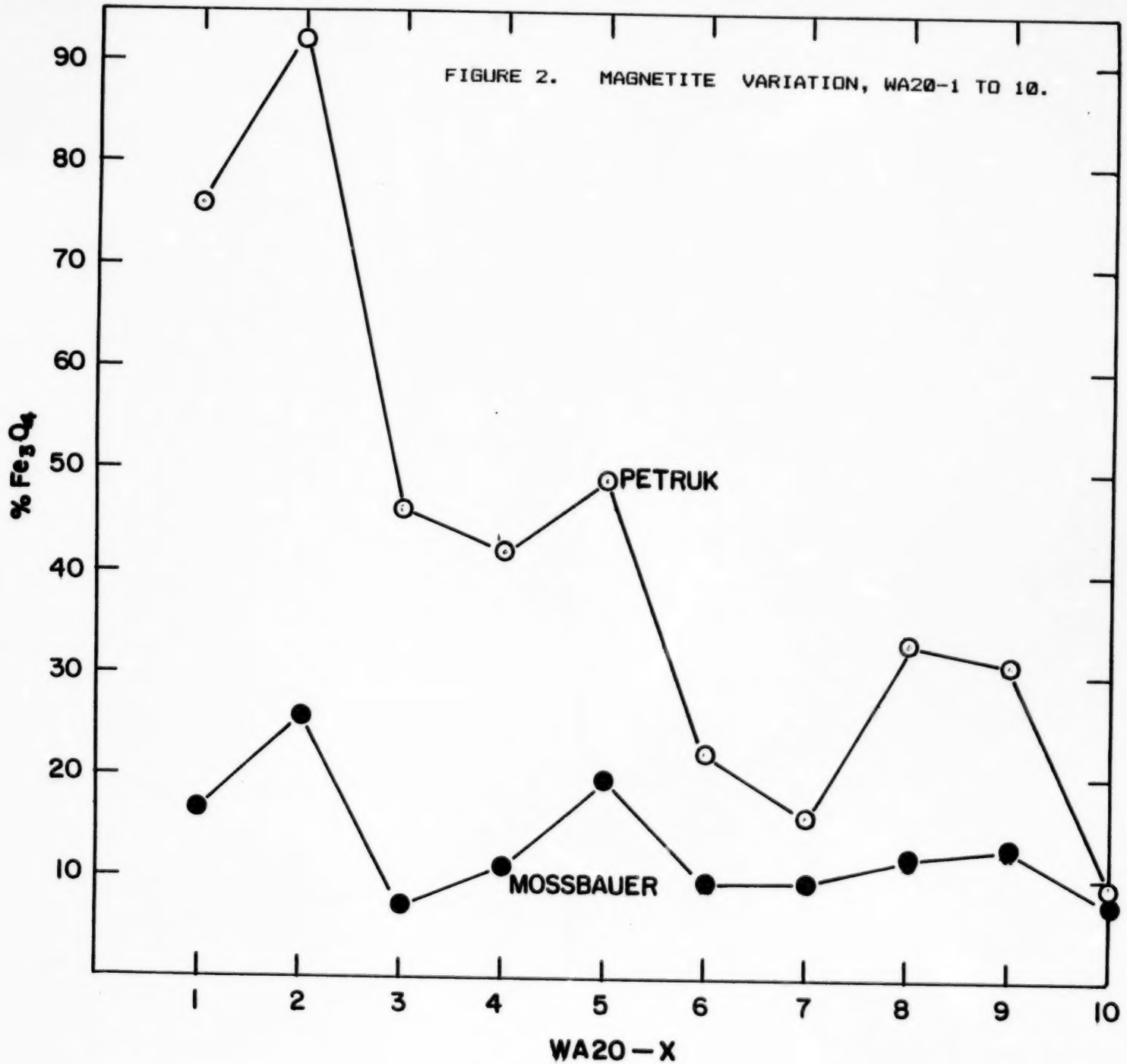
FIGURE 2. MAGNETITE VARIATION, WA20-1 TO 10.
90
80
70
60
50
40
30
20
10
% Fe_3O_4
PETRUK
MOSSBAUER
1
2
3
4
5
6
7
8
9
10
WA20 – X

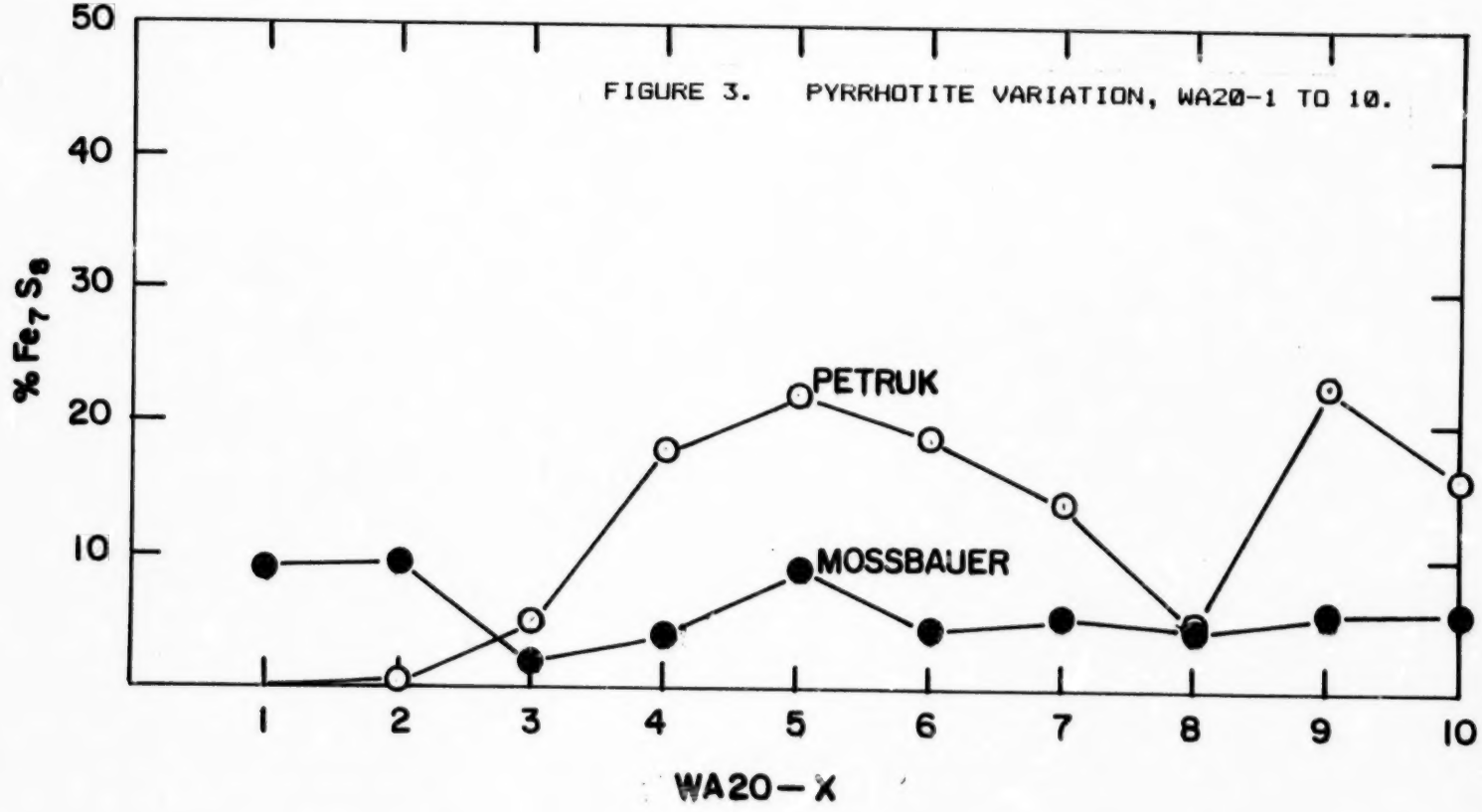

FIGURE 3. PYRRHOTITE VARIATION, WA20-1 TO 10.

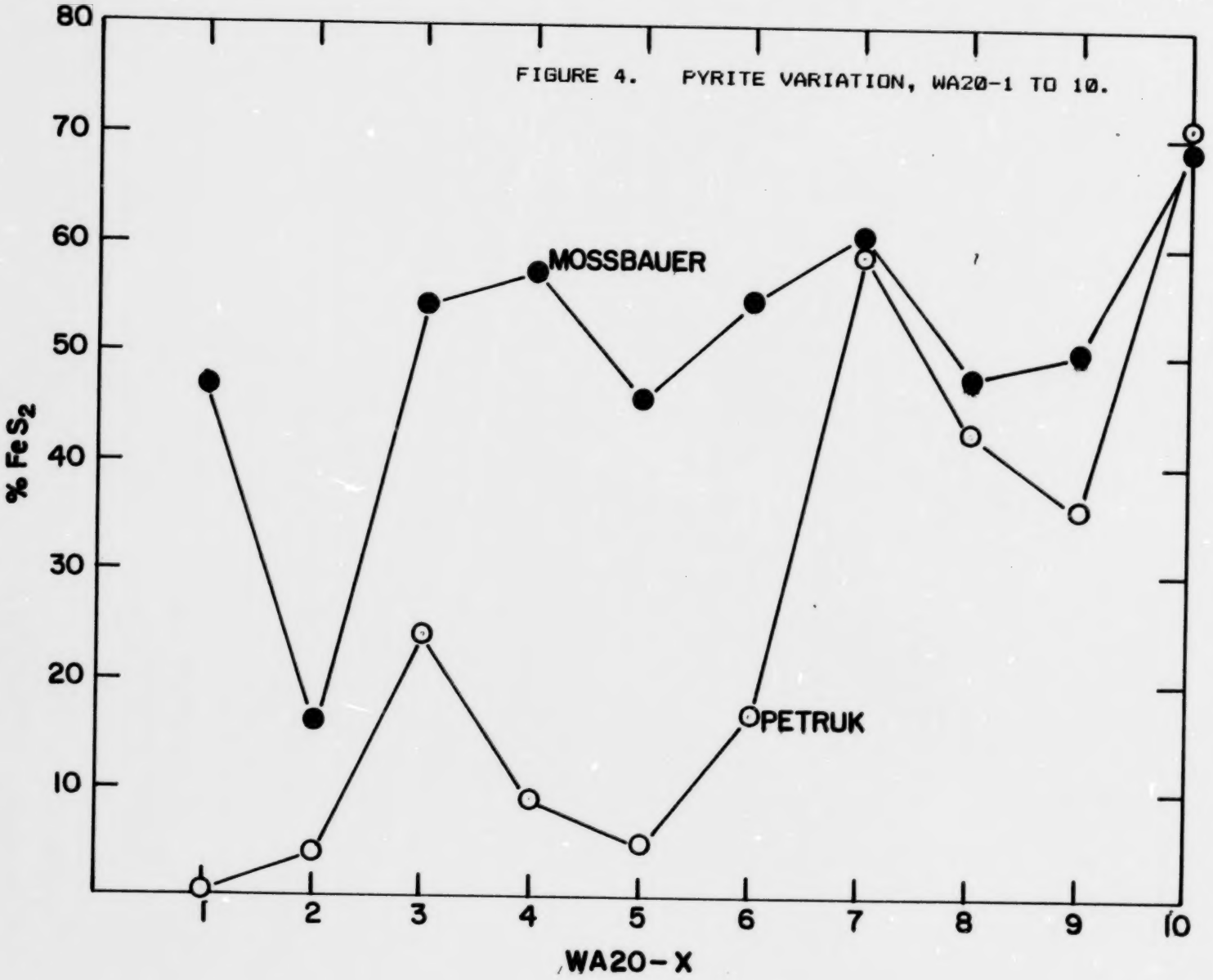

FIGURE 4. PYRITE VARIATION, WA20-1 TO 10.

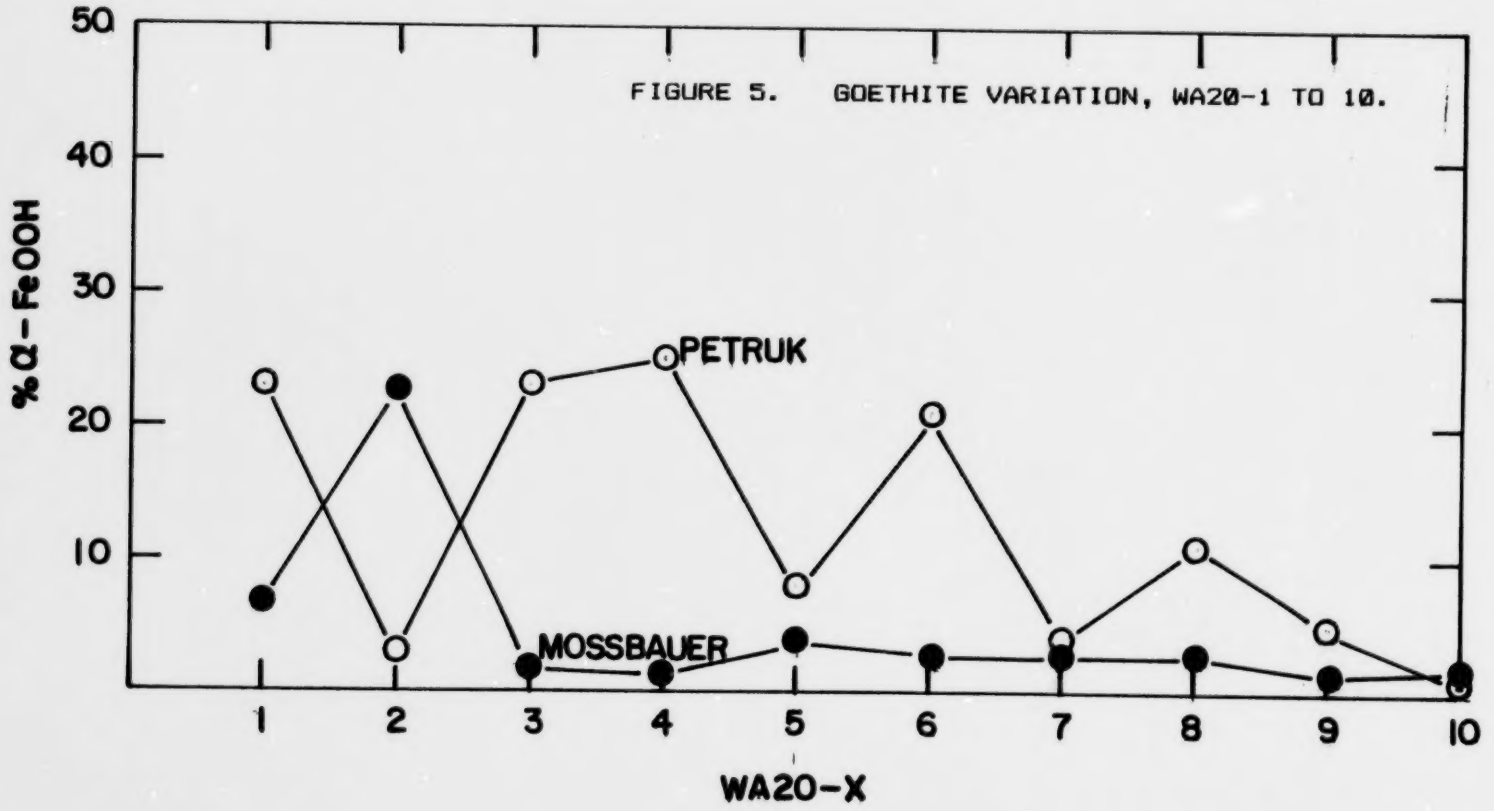

FIGURE 5. GOETHITE VARIATION, WA20-1 TO 10.